Formation of a Simple Hafnium Methylidene Complex by Reaction of Methyl Fluoride with Laser-Ablated Hafnium Atoms

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The methylidene hafnium complex ($CH_2{=}HfHF$) is formed by reaction of methyl fluoride with laser-ablated hafnium atoms and isolated in a solid argon matrix. The higher Hf−H and C−Hf stretching frequencies for $CH_2{=}HfHF$ than those of $CH_2{=}ZrHF$ are attributed to the shortened bonds for the heavier metal atom owing to relativistic effects. The singlet $CH_2{=}HfHF$ ground state molecule shows evidence of an α-hydrogen agnostic interaction. In contrast to the cases of Ti and Zr, the most likely initial $CH_3{-}HfF$ intermediate was not trapped in the matrix, as α-hydrogen shift led directly to the $CH_2{=}HfHF$ product.

Introduction

The high oxidation state transition metal alkylidene ($M{=}CR_1R_2$) and alkylidyne ($M{\equiv}CR$) complexes are of great interest not only because of their structure and bonding properties but also because of the catalytic activities of the complexes to metathesis of alkenes, alkynes, and cyclic compounds.[1,2] Such alkylidenes observed to date require bulky substituents to help stabilize the electron-deficient metal center. Transition metal methylidenes derived from simple halomethanes can serve as an ideal model system to study the nature of metal coordination chemistry including the effects of ligands and substituent modifications. Such compounds have been the subject of various theoretical studies,[3−6] but are inherently unstable due to lack of stabilizing resonance structures. Accordingly, stable group 4 metal alkylidene complexes are rare, although titanium alkylidene complexes have been proposed as intermediates in a variety of reactions.[1]

In recent studies, $CH_2{=}TiHF$ and $CH_2{=}ZrHF$ have been formed along with Grignard-type products ($CH_3{-}TiF$ and $CH_3{-}ZrF$) in reaction of the laser-ablated metal atoms and methyl fluoride in excess argon during condensation.[7,8] Interestingly enough, the reaction products of both metals isolated in a solid argon matrix form persistent photoreversible systems. In the titanium system, hydrogen migrates from the carbon to titanium atom ($CH_3{-}TiF \rightarrow CH_2{=}TiHF$) on UV irradiation, and vice versa on visible irradiation.[7] On the other hand, intersystem crossing between the singlet and triplet states of $CH_2{=}ZrHF$ appears to play a role on UV and visible irradiations.[8] These simple fluorine-substituted group 4 methylidene complexes provide model compounds for the heavily substituted versions previously investigated.[1,2]

The formation of $CH_2{=}TiHF$ and $CH_2{=}ZrHF$ along with the Grignard-type products raises a question whether hafnium, the last naturally available group 4 transition metal, also forms similar reaction products. Hafnium reacts readily with various compounds including CO,[9] NO,[10] H_2,[11,12] and C_2H_4[13] and shows the interesting relativistic effects of decreasing atomic size,[14−17] i.e., shortening of bonds to Hf with increasing vibrational frequencies of the products.[11] The first example of a hafnium alkylidene complex was formed in the reaction of $(CpP_2)HfCl_3$ and $C_6H_5CH_2K$ and was found to contain a Hf═C bond with 1.994 Å length.[18] In this paper, we report an investigation on the reaction of laser-ablated Hf atoms with methyl fluoride diluted in argon. The vibrational characteristics of this simple methylidene complex product are confirmed by isotopic substitution and DFT calculations.

Experimental and Computational Methods

Laser-ablated hafnium atoms (Johnson-Matthey) were reacted with CH_3F (Matheson), CD_3F (synthesized from CD_3Br and HgF_2), and $^{13}CH_3F$ (MSD Isotopes, 99%) in excess argon during condensation at 7 K using a closed-cycle He refrigerator (Air Products HC-2). The methods are previously described in detail elsewhere.[19,20] Concentrations of gas mixtures are

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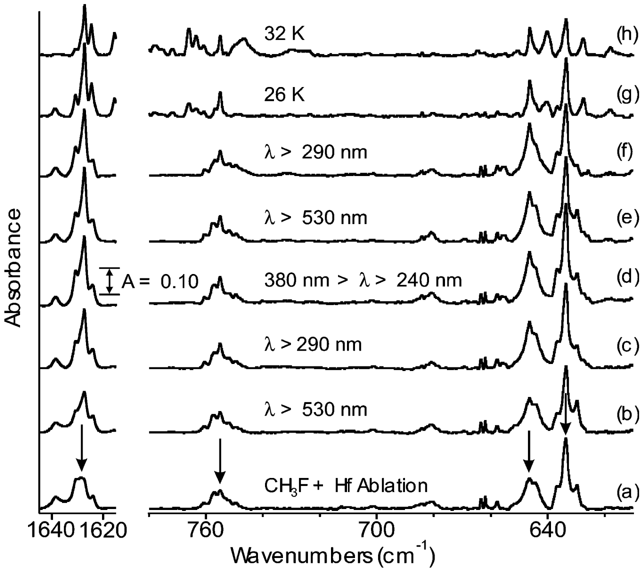

Figure 1. IR spectra in the regions of 1615−1645 and 610−780 cm^{-1} for laser-ablated Hf atoms co-deposited with Ar/CH_3F at 7 K. (a) Hf + 0.2% CH_3F in Ar co-deposited for 1 h, (b) after broad-band photolysis with a filter ($\lambda > 530$ nm) for 30 min, (c) after broad-band photolysis with a filter ($\lambda > 290$ nm) for 30 min, (d) after broad-band photolysis with a UV transmitting filter (240 nm $< \lambda <$ 380 nm) for 30 min, (e) after broad-band photolysis with a filter ($\lambda >$ 530 nm) for 30 min, (f) after broad-band photolysis with a filter ($\lambda > 290$ nm) for 30 min, (g) after annealing to 26 K, (h) after annealing to 32 K. An arrow indicates a product absorption.

typically 0.5% in argon. Samples were also irradiated by a combination of optical filters and a mercury arc lamp (175 W) and annealed. Complementary density functional theory (DFT) calculations were carried out using the Gaussian 98 package,[21] B3LYP density functional, 6-311+G(2d,p) basis sets for C, H, F, and SDD pseudopotential and basis set or LanL2DZ pseudopotential and basis set for Hf to provide a consistent set of vibrational frequencies and geometries for the reaction products. In calculation of the binding energy of a metal complex, the zero-point energy is included.

Results and Discussion

Figure 1 shows the IR spectra in the regions of 1615−1645 and 610−780 cm^{-1} for laser-ablated Hf atoms co-deposited with Ar/CH_3F at 7 K and their variation upon photolysis and annealing. In the relatively simple spectra, strong product absorptions observed at 1627.3, 755.1, 646.4, and 633.6 cm^{-1} are indicated by arrows. Irradiation with a broad-band Hg lamp and a filter ($\lambda > 530$ nm), following the co-deposition, leads to a slight decrease of the absorptions. On the other hand, irradiation with another filter ($\lambda > 290$ nm) brings about a 50% increase of the absorptions, and the following irradiation with a UV transmitting filter (240 nm $< \lambda <$ 380 nm) results in another 15% increase of the absorptions. In the continuing irradiation with $\lambda > 530$ nm and $\lambda > 290$ nm and following annealing, the absorptions weaken gradually.

These results suggest that Hf atom, electronically activated by UV irradiation, reacts with methyl fluoride located nearby in the matrix, resulting in increase of the product absorptions. Different trials show that irradiation with $\lambda < 320$ nm following co-deposition of methyl fluoride and the metal increases the absorption intensities, whereas irradiation with longer wavelength has minimal effects. On the other hand, prolonged irradiation slowly dissociates the product as shown in Figure 1. Dramatic changes and reversals in absorption intensities, similar to those in the Ti and Zr cases, are not observed in this study, and accordingly the spectrum is much simpler than found for the previous systems.[7,8]

The new absorptions at 1627.3, 755.1, 646.4, and 633.6 cm^{-1} show the same behavior upon irradiation and annealing, suggesting that they all arise from the same reaction product. Other than the major product absorptions, absorptions from the fragments of methyl fluoride, due to the vacuum UV emission by the high-energy metal atoms, are also observed, and the strongest absorptions (CH_2F and CHF) are shown in Figure 2. The identified fragments are basically the same as those in the previous Ti and Zr studies[7,8] and also consistent with the results of vacuum UV photolysis of methyl fluoride.[22]

As shown in Figure 2, ^{13}C substitution leads to negligible shifts of the strong absorption at 1627.3 cm^{-1}, whereas deuteration results in a large 461.4 cm^{-1} red shift in frequency (H/D isotopic ratio of 1.396), suggesting that it is the Hf−H stretching absorption. Absorptions of hafnium hydrides are also observed in the same frequency region.[11,12] This also indicates that, like in the cases of Ti and Zr,[7,8] C−H insertion by the metal atom readily occurs in the reaction of methyl fluoride with laser-ablated Hf atoms. Another strong absorption at 755.1 cm^{-1} shows isotope shifts of −20.9 and −114.8 cm^{-1} by ^{13}C and D substitutions ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.028 and 1.179). Based upon the frequency, considerable $^{12}C/^{13}C$ and H/D isotopic shifts, and calculation results, the absorption is assigned to the C−Hf stretching mode of the product. The much higher frequency than expected for a C−Hf single bond stretching frequency (below 600 cm^{-1}) suggests that the bond between C and Hf is in fact a double bond.

The strong absorption at 646.4 cm^{-1} shows isotope shifts of −0.4 and −108.9 cm^{-1} by ^{13}C and D substitutions ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.00 and 1.20) and probably originates from one of the CH_2 bending modes of the product. The absorption at 633.6 cm^{-1} exhibits very small ^{13}C and D isotope shifts of −1.4 and −11.8 cm^{-1}, indicating that it arises from the predominantly Hf−F stretching mode of the product. The present results show that the reaction product most likely contains Hf−H, C=Hf, CH_2, and Hf−F moieties, parallel to those of CH_2=TiHF and CH_2=ZrHF.[7,8]

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Table 1. Observed and Calculated Fundamental Frequencies of CH_2=HfHF in the Ground Electronic State[a]

	CH_2=HfHF				CD_2=HfDF				$^{13}CH_2$=HfHF			
description	observed	LanL	SDD	int.	observed	LanL	SDD	int.	observed	LanL	SDD	int.
ν_1 CH str.		3197	3180	0		2364	2351	1		3186	3169	1
ν_2 CH str.		2875	2922	11		2094	2128	4		2868	2915	11
ν_3 Hf−H str.	1631.0, **1627.3**	1666	1672	249	1167, **1165.9**	1183	1187	140	1630.8, **1627.3**	1666	1672	275
ν_4 CH_2 scis.		1332	1324	16		1029	1021	15		1324	1316	12
ν_5 C−Hf str.	757.2, **755.1**	768	740	48	645.2, **640.3**	686	661	33	735.5, **734.2**	747	719	51
ν_6 CH_2 wag	**646.4**, 644.4	694	692	116	537.5	543	512	96	**646.0**, 640.2	688	676	120
ν_7 Hf−F str.	633.6	645	636	189	621.8	631	619	134	632.2	645	635	179
ν_8 CHfH bend		572	563	30		429	423	26	547.2	571	561	25
ν_9 CH_2 twist		432	436	42		308	311	17		432	436	35
ν_{10} CH_2 rock		363	324	5		291	267	4		359	321	18
ν_{11} HCHfH distort		284	249	93		209	184	53		284	248	87
ν_{12} CHfF bend		140	129	21		121	109	10		138	128	17

[a] Frequencies and intensities are in cm^{-1} and km/mol. Intensities are all calculated values at B3LYP/6-311+G(2d,p)/SDD. The stronger absorptions are bolded.

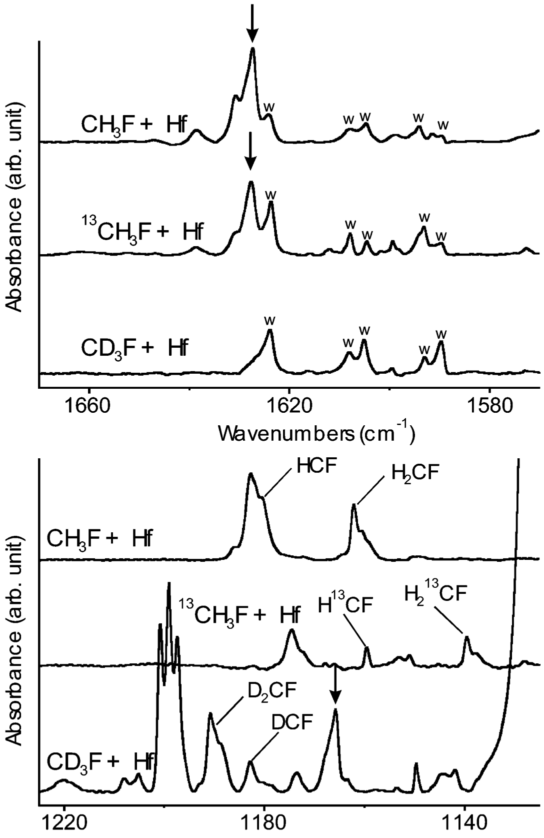

Figure 2. IR spectra in the regions of 1570−1670 and 1125−1225 cm^{-1} after UV (240 nm < λ < 380 nm) photolysis following co-deposition of laser-ablated Hf atoms with methyl fluoride isotopomers diluted in Ar at 7 K. An arrow indicates a product absorption. The absorptions by fragments of methyl fluoride are also identified with the name of species, and water absorptions are indicated, as well.

These spectroscopic characteristics suggest that the major product absorptions observed in this study arise from CH_2=HfHF, which is consistent with the observed vibrational characteristics and is also an energetically favorable product molecule. The observed frequencies are compared with the calculated values in Table 1, and very good agreement is found for both SDD and LANL2DZ pseudopotential and basis sets for the heavy metal.

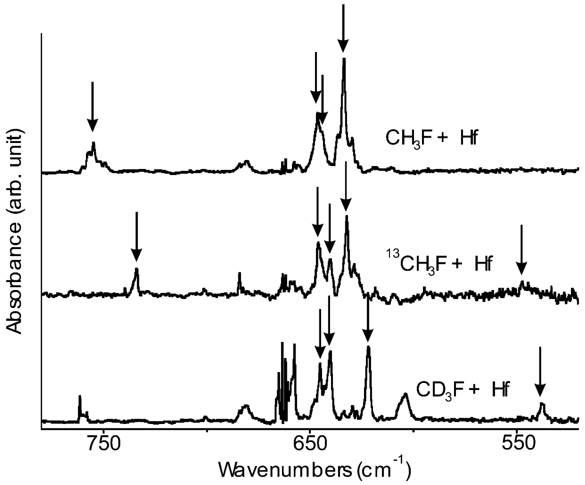

Figure 3. IR spectra in the region of 520−780 cm^{-1} for laser-ablated Hf atoms co-deposited with methyl fluoride isotopomers diluted in Ar at 7 K.

The present results indicate that, like Ti and Zr, Hf also forms a methylidene complex. On the other hand, unlike the previous cases,[7,8] the initial Grignard-type CH_3−HfF intermediate is not identified in the infrared spectrum. In previous studies, it is shown that the Grignard-type product readily transforms via hydrogen shift to the methylidene product on UV irradiation. Figure 4 compares spectra for Ti, Zr, and Hf where the methylidene products are marked I. Notice that the yield of CH_3−TiF is large and the CH_3−ZrF absorptions (labeled III) are weak on sample deposition, but there is no evidence for CH_3−HfF. On UV (240−380 nm) irradiation, the CH_2=TiHF and CH_2=ZrHF methylidenes both increase with decrease of the absorptions of CH_3−MF. In the following visible (λ > 530 nm) irradiation, the absorptions from CH_3−TiF increase again, whereas the absorptions from CH_3−ZrF do not recover, regardless of the wavelength, and CH_3−HfF is not produced. The absorptions marked IV with Ti are due to $(CH_3)_2TiF_2$, which is formed by the addition of CH_3F to CH_3−TiF.[7] Such a product is not observed for Zr and Hf.

Calculations show that CH_3−TiF and CH_3−ZrF in the triplet states are 22 and 5 kcal/mol more stable than the corresponding methylidene products in their singlet ground states.[7,8] On the other hand, the energies of singlet CH_2=HfHF and triplet CH_3−HfF are essentially

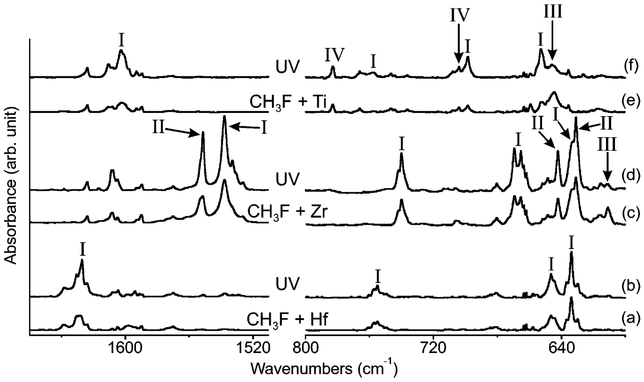

Figure 4. IR spectra of Ti, Zr, and Hf + CH_3F in the regions of 600−800 and 1510−1660 cm^{-1}. (a) Hf + 0.5% CH_3F in Ar co-deposited for 1 h and (b) after UV (240 nm $< \lambda <$ 380 nm) irradiation for 20 min. (c) Zr + 0.5% CH_3F in Ar co-deposited for 1 h and (d) after UV (240 nm $< \lambda <$ 380 nm) irradiation for 20 min. (e) Ti + 0.2% CH_3F in Ar co-deposited for 1h and (f) after UV (240 nm $< \lambda <$ 380 nm) irradiation for 10 min. I, II, III, and IV identify the absorptions of $CH_2{=}MHF$, $CH_2{=}ZrHF$ in a second argon matrix configuration, CH_3ZrF or CH_3TiF, and $(CH_3)_2TiF_2$, respectively.

the same at the present level of theory, and we expect the $CH_3{-}HfF$ intermediate first formed in exothermic reaction 1 to spontaneously rearrange to $CH_2{=}HfHF$ by α-H shift, a well-known process in organometallic chemistry.[23]

$$\mathrm{Hf} + \mathrm{CH_3F} \rightarrow (\mathrm{CH_3{-}HfF}) \qquad \Delta E = -100\ \mathrm{kcal/mol} \tag{1}$$

Collision of the transition metal atom on the fluorine side of methyl fluoride most likely leads to formation of the Grignard-type product.[7,8] One possibility is that $CH_3{-}HfF$ formed in the reaction of methyl fluoride with vaporized Hf atoms quickly transforms to the methylidene complex under light emitted from the plume of laser ablation in the process of co-deposition, leaving a too small amount of the product to be identified in the infrared spectrum. Another possibility is that the actual energy of $CH_3{-}HfF$ is slightly higher than that of $CH_2{=}HfHF$. As a result, the Grignard-type product produced in reaction of methyl fluoride and Hf atoms spontaneously transforms to the methylidene complex during relaxation in the matrix. In any case the $CH_3{-}HfF$ product of reaction 1 is probably produced with substantial excess energy, and this is sufficient to overcome any activation barrier for reaction 2.

$$(\mathrm{CH_3{-}HfF}) \rightarrow \mathrm{CH_2{=}HfHF} \tag{2}$$

The optimized geometry of $CH_2{=}HfHF$ is illustrated along with those of $CH_2{=}TiHF$ and $CH_2{=}ZrHF$ in Figure 5, and the geometrical parameters of $CH_2{=}HfHF$ are compared with the other methylidene complexes in Table 2. All of the methylidene complexes in the singlet ground state have nonplanar (C_1) structures with the carbon and metal atom centers both serving as apexes of trigonal pyramids. Among the methylidene complexes in the singlet ground states, $CH_2{-}HfHF$ has the most nonplanar structure. On the other hand, all three methylidene complexes have a planar (C_s) structure in their lowest triplet states, which lie 13−20 kcal/mol above the singlet states. We note that our B3LYP calculated Hf=C bond length, 1.981 Å, is very near that measured for $(CpP_2)Hf(CHPh)Cl$, at 1.994 Å.[18] Values of 1.884, 2.024, and 1.994 Å for M=C double bond lengths are typical of the alkylidene complexes for M = Ti, Zr, and Hf, respectively.[18,26,27]

Table 2. Geometrical Parameters and Physical Constants of Ground Singlet State $CH_2{=}TiHF$, $CH_2{=}ZrHF$, and $CH_2{=}HfHF$[a]

parameter	$CH_2{=}TiHF$	$CH_2{=}ZrHF$	$CH_2{=}HfHF$
r(C−H)	1.084, 1.114	1.085, 1.114	1.085, 1.109
r(C−M)	1.812	1.966	1.981
r(M−H)	1.731	1.883	1.875
r(M- - -H′)	2.192, 2.813	2.365, 2.959	2.448, 2.939
r(M−F)	1.786	1.947	1.934
∠HCH	114.2	112.3	112.1
∠CMF	119.0	114.3	112.4
∠CMH	111.7	107.6	105.6
∠HMF	124.4	119.9	116.4
∠HCM	94.0, 151.4	96.3, 150.4	101.0, 145.4
Φ(HCMH)	158.8, −11.7	143.0, −23.2	135.7, −27.7
Φ(HCMF)	2.4, −168.1	7.1, −159.1	7.8, −135.7
sym	C_1	C_1	C_1
q(C)[b]	−0.61	−0.89	−0.76
q(H)[b,c]	−0.12, 0.10, 0.15	−0.23, 0.09, 0.12	−0.21, 0.09, 0.21
q(M)[b]	0.89	1.36	1.18
q(F)	−0.41	−0.46	−0.42
μ[d]	1.60	3.28	3.81
state[e]	^1A	^1A	^1A
ΔE[f]	−66	−99	−99

[a] Bond lengths and angles are in Å and deg. All calculations were done at the B3LYP/6-311+G(2d,p)/SDD level. [b] Mulliken atomic charge. [c] Numbers are in the order from the closest one to the metal atom to the farthest. [d] Molecular dipole moment in D. [e] Electronic state. [f] Binding energies in kcal/mol.

It is noteworthy in Figure 5 that one of the methylene hydrogen atoms is located unusually close to the metal atom of the methylidenes in the singlet ground state, resulting in the distorted methylene group. Evidently a strong agostic interaction exists between the metal atom and one of the α-hydrogen atoms in all the methylidene complexes in the ground state.[26−28] The three-center C−H···M agostic interactions occur quite frequently in electronically unsaturated organometallic complexes. The strength (typically 10−15 kcal/mol) and geometry of these bonds depend on the energy and disposition of the vacant metal orbitals relative to the C−H bonding orbitals and the steric effects imposed to the linkage. While these interactions are normally considered benign, they still can cause a significant distortion within the ligand including bending at CH_2 and lengthening of the C−H bond. On the basis of the M···H interatomic distances and H−C−M angles (r(Ti−H), r(Zr−H), and r(Hf−H) are 2.192, 2.365, and 2.448 Å, and ∠HCTi, ∠HCZr, and ∠HCHf are 94.0°,

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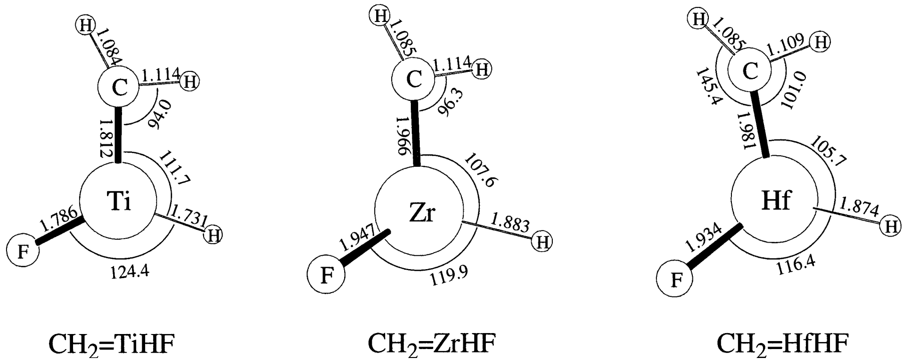

Figure 5. Optimized molecular structures (B3LYP/6-311+G(2d,p)/SDD) for CH_2═TiHF, CH_2═ZrHF, and CH_2═HfHF. The bond lengths and angles are in Å and deg. The methylene group is noticeably distorted, and one of the methylene hydrogen atoms is very close to the metal atom in the CH_2═TiHF, CH_2═ZrHF, and CH_2═HfHF singlet state species, indicating that there is strong agostic interaction.

Table 3. M−H and C−M Stretching Frequencies of CH_2═TiHF, CH_2═ZrHF, and CH_2═HfHF in the Singlet Ground States[a]

M	$^{12}CH_2$═MHF	CD_2═MDF	$^{13}CH_2$═MHF	mode
Ti	1602.8	1158.6	1602.8	Ti−H str.
	757.8	644.9	748.4	C−Ti str.
Zr	1537.8	1104.3	1537.8	Zr−H str.
	740.0	641.8	721.5	C−Zr str.
Hf	1627.3	1165.9	1627.3	Hf−H str.
	755.1	640.3	734.2	C−Hf str.

[a] Frequencies are all solid argon values in cm^{-1}.

96.3°, and 101.0°), the agostic interaction decreases in the order of CH_2═TiHF, CH_2═ZrHF, and CH_2═HfHF.

The measured metal−hydrogen and carbon−metal stretching frequencies of CH_2═TiHF, CH_2═ZrHF, and CH_2═HfHF in the singlet ground states are listed in Table 3. It is notable that the hydrogen stretching frequencies of CH_2═HfHF isotopomers are much higher than those of CH_2═ZrHF isotopomers and also slightly higher than those of CH_2═TiHF isotopomers. The carbon−metal stretching frequencies of CH_2═HfHF isotopomers are also higher or comparable to those of CH_2═ZrHF isotopomers. It is also interesting that the calculated Hf−H and Hf−F bond lengths are in fact shorter than the Zr−H and Zr−F bond lengths, respectively, as listed in Table 2. The higher stretching frequencies and shorter bond lengths in the Hf methylidene complex are attributed to the larger relativistic bond-length contraction for Hf predicted by Pyykko et al.[14−17] Similar effects were found for the TiH_4, ZrH_4, and HfH_4 tetrahydrides.[11,12]

Conclusions

A transition metal methylidene complex CH_2═HfHF is formed in the reaction of laser-ablated Hf atoms with methyl fluoride in excess argon during condensation at 7 K, which is apparently the only major Hf-methyl fluoride complex trapped in the matrix. Dramatic reversible photochemical processes, similar to those found with Ti and Zr,[7,8] are not observed in the Hf system, but the major product absorptions grow about 65% on UV (240 nm < λ < 320 nm) irradiation. The molecular structure of CH_2═HfHF and those of CH_2═TiHF and CH_2═ZrHF show evidence of α-agostic interaction between the metal atom and one of the α-hydrogen atoms in the ground singlet state. The Hf−H stretching frequency of CH_2═HfHF is higher than the corresponding Ti−H and Zr−H frequencies, and the Hf−H and Hf−F bonds are shorter than the Zr−H and Zr−F bonds, evidence of lanthanide contraction by relativistic effects for hafnium.[17] Group 4 transition metal atoms readily form methylidene complexes by reaction with methyl fluoride.

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